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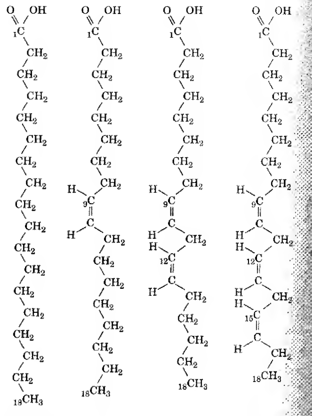
1. LIPID CLASSIFICATION

***Lipids** (Greek: lipos, fat) are substances of biological origin that are soluble in organic solvents such as chloroform and methanol but are only sparingly soluble, if at all, in water.* Hence, they are easily separated from other biological materials by extraction into organic solvents and may be further fractionated by such techniques as adsorption chromatography, thin layer chromatography, and reverse-phase chromatography (Section 5-3E). Fats, oils, certain vitamins and hormones, and most nonprotein membrane components are lipids. In this section, we discuss the structures and physical properties of the major classes of lipids.

A. Fatty Acids

***Fatty acids** are carboxylic acids with long-chain hydrocarbon side groups (Fig. 11-1).* They are rarely free in nature but, rather, occur in esterified form as the major components of the various lipids described in this chapter. The more common biological fatty acids are listed in Table 11-1. In higher plants and animals, the predominant fatty acid residues are those of the C_{16} and C_{18} species **palmitic, oleic, linoleic,** and **stearic acids.** Fatty acids with <14 or >20 carbon atoms are uncommon. *Most fatty acids have an even number of carbon atoms because they are usually biosynthesized by the concatenation of C_2 units (Section 23-4C).* Over half of the fatty acid residues of plant and animal lipids are unsaturated (contain double bonds) and are often



Stearic acid **Oleic acid** **Linoleic acid** **α-Linolenic acid**

FIGURE 11-1. The structural formulas of some C_{18} fatty acids. The double bonds all have the cis configuration.

TABLE 11-1. **The Common Biological Fatty Acids**

Symbol[a]	Common Name	Systematic Name	Structure	mp (°C)
Saturated fatty acids				
12:0	Lauric acid	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	44.2
14:0	Myristic acid	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	52
16:0	Palmitic acid	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	63.1
18:0	Stearic acid	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	69.6
20:0	Arachidic acid	Eicosanoic acid	$CH_3(CH_2)_{18}COOH$	75.4
22:0	Behenic acid	Docosanoic acid	$CH_3(CH_2)_{20}COOH$	81
24:0	Lignoceric acid	Tetracosanoic acid	$CH_3(CH_2)_{22}COOH$	84.2
Unsaturated fatty acids (all double bonds are cis)				
16:1	Palmitoleic acid	9-Hexadecenoic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	−0.5
18:1	Oleic acid	9-Octadecenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13.4
18:2	Linoleic acid	9,12-Octadecadienoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	−9
18:3	α-Linolenic acid	9,12,15-Octadecatrienoic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	−17
18:3	γ-Linolenic acid	6,9,12-Octadecatrienoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_3(CH_2)_3COOH$	
20:4	Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	−49.5
20:5	EPA	5,8,11,14,17-Eicosapentanoic acid	$CH_3CH_2(CH{=}CHCH_2)_5(CH_2)_2COOH$	−54
24:1	Nervonic acid	15-Tetracosenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$	39

[a] Number of carbon atoms : Number of double bonds.

Source: Dawson, R.M.C., Elliott, D.C., Elliott, W.H., and Jones, K.M., *Data for Biochemical Research* (3rd ed.), Chapter 8, Clarendon Press (1986).

polyunsaturated (contain two or more double bonds). Bacterial fatty acids are rarely polyunsaturated but are commonly branched, hydroxylated, or contain cyclopropane rings. Unusual fatty acids also occur as components of the oils and **waxes** (esters of fatty acids and long-chain alcohols) produced by certain plants.

The Physical Properties of Fatty Acids Vary with Their Degree of Unsaturation

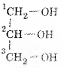
Table 11-1 indicates that the first double bond of an unsaturated fatty acid commonly occurs between its C9 and C10 atoms counting from the carboxyl C atom (a Δ^9- or 9-double bond). In polyunsaturated fatty acids, the double bonds tend to occur at every third carbon atom towards the methyl terminus of the molecule (such as $-CH{=}CH{-}CH_2{-}CH{=}CH{-}$). Double bonds in polyunsaturated fatty acids are almost never conjugated (as in $-CH{=}CH{-}CH{=}CH{-}$). Triple bonds rarely occur in fatty acids or any other compound of biological origin.

Saturated fatty acids are highly flexible molecules that can assume a wide range of conformations because there is relatively free rotation about each of their C—C bonds. Nevertheless, their fully extended conformation is that of minimum energy because this conformation has the least amount of steric interference between neighboring methylene groups. The melting points (mp) of saturated fatty acids, like those of most substances, increase with molecular mass (Table 11-1).

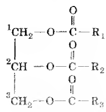
Fatty acid double bonds almost always have the cis configuration (Fig. 11-1). This puts a rigid 30° bend in the hydrocarbon chain of unsaturated fatty acids that interferes with their efficient packing to fill space. The consequent reduced van der Waals interactions cause fatty acid melting points to decrease with their degree of unsaturation (Table 11-1). Lipid fluidity likewise increases with the degree of unsaturation of their component fatty acid residues. This phenomenon, as we shall see in Section 11-3B, has important consequences for membrane properties.

B. Triacylglycerols

The fats and oils that occur in plants and animals consist largely of mixtures of **triacylglycerols** (also referred to as **triglycerides or neutral fats**). *These nonpolar, water-insoluble substances are fatty acid triesters of* **glycerol**:



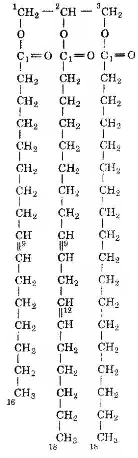
Glycerol



Triacylglycerol

Triacylglycerols function as energy reservoirs in animals and are therefore their most abundant class of lipids even though they are not components of biological membranes.

Triacylglycerols differ according to the identity and placement of their three fatty acid residues. The so-called **simple triacylglycerols** contain one type of fatty acid residue and are named accordingly. For example, **tristearoylglycerol** or **tristearin** contains three stearic acid residues, whereas **trioleoylglycerol or triolein** has three oleic acid residues. The more common **mixed triacylglycerols** contain two or three different types of fatty acid residues and are named according to their placement on the glycerol moiety.



1-Palmitoleoyl-2-linoleoyl-3-stearoyl-glycerol

Fats and oils (which differ only in that fats are solid and oils are liquid at room temperature) are complex mixtures of simple and mixed triacylglycerols whose fatty acid compositions vary with the organism that has produced them. Plant oils are usually richer in unsaturated fatty acid residues than are animal fats, as the lower melting points of oils imply.